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Calibration of Liquid-in-Glass Thermometers

U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

THE NATIONAL BUREAU OF STANDARDS

The National Bureau of Standards is a principal focal point in the Federal Government for assuring maximum application of the physical and engineering sciences to the advancement of technology in industry and commerce. Its responsibilities include development and maintenance of the national standards of measurement, and the provisions of means for making measurements consistent with those standards; determination of physical constants and properties of materials; development of methods for testing materials, mechanisms, and structures, and making such tests as may be necessary, particularly for government agencies; cooperation in the establishment of standard practices for incorporation in codes and specifications; advisory service to government agencies on scientific and technical problems; invention and development of devices to serve special needs of the Government; assistance to industry, business, and consumers in the development and acceptance of commercial standards and simplified trade practice recommendations; administration of programs in cooperation with United States business groups and standards organizations for the development of international standards of practice; and maintenance of a clearinghouse for the collection and dissemination of scientific, technical, and engineering information. The scope of the Bureau's activities is suggested in the following listing of its four Institutes and their organizational units.

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Institute for Applied Technology. Textiles and Apparel Technology Center. Building Research. Industrial Equipment. Information Technology. Performance Test Development. Instrumentation. Transport Systems. Office of Technical Services. Office of Weights and Measures. Office of Engineering Standards. Office of Industrial Services.

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*NBS Group, Joint Institute for Laboratory Astrophysics at the University of Colorado.
**Located at Boulder, Colorado.

UNITED STATES DEPARTMENT OF COMMERCE • Luther H. Hodges, *Secretary*
NATIONAL BUREAU OF STANDARDS • A. V. Astin, *Director*

Calibration of Liquid-in-Glass Thermometers

James F. Swindells

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Foreword

The liquid-in-glass thermometer is probably the most widely used temperature measuring device in both science and industry. In spite of its fragile nature, its relative simplicity makes this type of thermometer singularly attractive where reliable temperature measurements are required but where the highest attainable accuracy is not necessary.

The liquid-in-glass thermometer is not an entirely foolproof instrument, however. If the user is to realize the accuracy of which his thermometer is capable, and to recognize its inherent limitations as well, he must have, in additon to its calibration, some knowledge of the behavior to be expected of such a thermometer. It is the purpose of this Monograph to emphasize the important features of good practice in the design and use of liquid-in-glass thermometers, and to describe the techinques used by the National Bureau of Standards in their calibration. This information is intended to be of value not only to those who wish to submit thermometers to the Bureau for calibration, but also to manufacturers, to other standards laboratories, and to those who wish to calibrate their own instruments.

A. V. Astin, *Director.*

Contents

	Page
Foreword	III
1. Introduction	1
2. Thermometer calibration services	1
2.1. Kinds of thermometers accepted for calibration	1
2.2. Reports of calibration	2
2.3. General instructions to applicants for tests	2
a. Initial arrangements	2
b. Shipping instructions	2
3. Definitions	5
4. Temperature scales and standards	6
5. Calibration procedures	7
5.1. Equipment	7
a. Ice bath	7
b. Steam bath	7
c. Comparison liquid baths	7
5.2. Number and choice of test points	10
5.3. Determination of scale corrections	10
5.4. Corrections for emergent stem	11
a. Measurement of emergent-stem temperature	11
b. Formula for total-immersion thermometers	12
c. Formula for partial-immersion thermometers	13
d. Formula for calorimeter thermometers	13
e. Formula for Beckmann thermometers	13
6. Common thermometers and factors affecting their use	14
6.1. Total-immersion thermometers	14
6.2. Partial-immersion thermometers	15
6.3. Low-temperature thermometers	15
6.4. Beckmann thermometers	16
6.5. Calorimeter thermometers	17
7. Thermometer design	17
7.1. Materials of construction	18
7.2. Scale design and workmanship	18
7.3. Scale dimensions	18
7.4. Reference point on scale	19
7.5. Marking of partial-immersion thermometers	19
8. Special notes	19
8.1. Glass changes	19
a. Temporary changes	20
b. Permanent changes	20
8.2. Pressure effects	21
8.3. Lag	21
8.4. Separated columns	22
9. References	23

Calibration and Use of Liquid-in-Glass Thermometers

James F. Swindells

This Monograph, which supersedes Circular 600, contains information of general interest to both manufacturers and users of liquid-in-glass thermometers, as well as those who wish to calibrate thermometers or submit them to the National Bureau of Standards for calibration. Instructions are provided for applicants requesting calibration services, and the techniques and equipment used in the calibration procedures are described. Important elements of thermometer design are discussed, and factors affecting the use of common types of liquid-in-glass thermometers are included together with tables of tolerances and reasonably attainable accuracies. The calculation of corrections for the temperature of the emergent stem is given in detail for various types of thermometers and conditions of use.

1. Introduction

It is the responsibility of the National Bureau of Standards to establish, maintain, and assume custody of the Nation's standards of physical measurement. One important activity under this responsibility is the accurate reproduction of the International Practical Temperature Scale as a basis for the uniform measurement of temperature throughout the scientific and industrial activities of the United States. To this end the Bureau accepts for calibration with reference to this scale selected types of temperature-measuring instruments [1] [1] for use as reference or working standards where precise-temperature measurements are required. Less precise types of instruments are not accepted, nor are the more routine calibrations performed in cases where such work can be done in qualified commercial testing laboratories. This Monograph describes the practices employed at the Bureau in the calibration of acceptable types of liquid-in-glass thermometers. The information is intended for those who wish to submit thermometers for calibration or who have occasion to use thermometers calibrated at the Bureau.

Important features of good practice in the use of liquid-in-glass thermometers are emphasized to assure realization of the accuracy of which thermometers are capable, as well as to point out their inherent limitations.

In this Monograph, the material presented in Circular 600 has been somewhat expanded and brought up to date. The rearrangement of the material is intended to inform the reader immediately of the Bureau's calibration services and how to make use of them, with the detailed description of calibration methods and discussions of topics in thermometry coming later.

2. Thermometer Calibration Services

The liquid-in-glass thermometer, discussed in this Monograph, is one of many types of precise instruments and standards for which calibration services are offered by the NBS. A complete listing is found in NBS Miscellaneous Publication 250.

As services are initiated or discontinued, or as fees are changed, announcements will appear in the Federal Register. Major changes in these will be noted in the Standards and Calibration column of the NBS Technical News Bulletin. The Bureau also plans to issue periodical listings of such changes. To be placed on a mailing list to receive these inserts as they are issued, a request should be addressed to The Office of Technical Information, National Bureau of Standards, Washington, D.C., 20234.

2.1. Kinds of Thermometers Accepted for Calibration

Liquid-in-glass thermometers include a wide variety of types, not all of which are accepted for test. In general, considerations of design, intended use, and probable stability of the thermometer indications are the principal factors governing acceptability for test. Thermometers belonging to the large and varied group which may be classed as laboratory or "chemical" thermometers are regularly accepted. These may be of the etched-stem or enclosed scale (Einschluss) type. Other acceptable types include such special-purpose thermometers as Beckmanns and calorimeter thermometers. Thermometers of the so-called industrial or mechanical types, with special mountings for their various intended uses, can be accepted for test only when their construction permits testing with the equipment available.

[1] Figures in brackets indicate the literature references at the end of this Monograph.

Ordinary household or meteorological thermometers will not, in general, be accepted unless the scale is graduated on the glass stem itself and the thermometer can be readily detached from its mounting for insertion in a testing bath.

Every thermometer submitted must be uniquely identified by a serial number and must pass a preliminary examination for details of construction before being finally accepted for test. The examination is made with optical aid (15 or 20 ×) for fineness and uniformity of graduation, cleanness of the mercury and capillary bore, and freedom from moisture, gas bubbles, and cracks in the glass. Among other possible defects detected in other ways, are omission of gas filling where needed, insufficient annealing and misnumbered graduations. A complete listing of all possible defects is not practicable. When serious defects are found the thermometer is returned untested.

2.2. Reports of Calibration

A Report of Calibration issued by the Bureau for a liquid-in-glass thermometer, in addition to giving the results of the calibration, may be taken as an indication that the thermometer is free from serious defects of design, material, or workmanship, as discussed in section 7. Except in special instances, a Report of Calibration is issued only when the thermometer has been calibrated at a sufficient number of points to provide reasonable assurance that the corrections obtained at the temperatures of calibration can be applied, with interpolation and extrapolation, throughout the whole scale (see sec. 5.2).

In addition to the scale corrections listed with the temperatures of calibration, the Report contains an estimate of the uncertainties associated with the corrections. The Report will also show the following information: the manufacturer's identification markings and numbers, the agency or firm for which the calibration was made, the NBS test number and date of test, and explanatory notes necessary to define the conditions under which the results of test are applicable. When necessary, the Report is accompanied by a sheet showing how to calculate the correction for emergent stem. If the thermometer is of the metastatic (Beckmann) type, the Report will be accompanied by a table of setting factors to enable the user to apply the calibration results when the thermometer is used with a setting other than that for which the corrections are given. Figure 1 shows the face of a sample Report and figure 2 shows the back of the same Report.

It should be emphasized that the estimates of error assigned to the scale corrections do not assure the user of this accuracy in a temperature measurement. Care must be taken that the thermometer bulb is at the temperature of the medium whose temperature is to be measured. This involves considerations of heat transfer from the medium to the bulb and heat conduction along the thermometer stem. Any departure from the conditions under which the corrections were obtained in calibration may significantly change the values of the corrections. Conditions of immersion are particularly important (see sec. 6), and even a change in the pressure to which the bulb is exposed may require an additional correction (sec. 8.2).

Some of the reasons why a thermometer may be denied a Report of Calibration are summarized as follows:

(a) Defective design or workmanship.
(b) Omission, where required, of ice point or other reference point.
(c) Part of graduated scale not usable.
(d) Defects in scale graduation or numbering.
(e) Omission of required marking on partial-immersion thermometers.
(f) Unsuitable bulb glass or inadequate annealing.
(g) Inadequate gas filling.
(h) Excessive scale error.

Details of good design and workmanship are discussed in section 7.

2.3. General Instructions to Applicants for Tests

Tests in accord with the policies of the National Bureau of Standards, and of the types indicated in the fee schedules as published in the "Federal Register", will be undertaken. If need arises for a special test, not listed in the fee schedule but of a similar nature, the Bureau should be consulted. If the required measurements appear feasible, and, in the opinion of the Bureau, sufficiently important to justify the work, such tests will be undertaken for a special fee determined by the nature of the work. In all requests the following procedures and information are pertinent.

a. Initial Arrangements

A letter or purchase order, stating the tests desired and referring to the appropriate section and subsections of the fee schedule, should be sent to the Bureau prior to any shipment. The purpose of this requirement is to determine whether or not the Bureau will undertake the test and to insure correct procedure in reporting, shipping, and billing. In the case of routine or periodic tests, of a type made previously for the requester, this letter may be sent at the time shipment is made. In general, the purpose of the test and the manner in which the results are to be used should be stated. If the thermometer submitted has been previously calibrated by the Bureau, reference should be made to the former test number. A test number will be assigned by the Bureau to each project, and this test number must be referred to in all subsequent communications.

b. Shipping Instructions

Shipping charges, both to and from the Bureau, must be assumed by the applicant. Return shipments are made by the Bureau in accordance with

FORM NBS-186
(7-1-63)

U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS
WASHINGTON, D.C. 20234

NATIONAL BUREAU OF STANDARDS

REPORT OF CALIBRATION

LIQUID-IN-GLASS THERMOMETER

Tested for: National Bureau of Standards
Division 221, Section 01

Marked: Surety 198692

Range: -2 to +102 °C in 0.2°

Thermometer Reading	Correction
- 0.06 °C	+0.06 °C
10.00	+ .08
20.00	+ .14
30.00	+ .10
40.00	+ .04
50.00	+ .04
60.00	+ .04
70.00	+ .06
80.00	+ .06
90.00	+ .06
100.00	+ .04

If the correction is + the true temperature is higher than the indicated temperature; if the correction is - the true temperature is lower than the indicated temperature. To use the corrections properly, reference should be made to the notes marked by asterisks on the reverse of this sheet.

Estimated uncertainties in the above corrections do not exceed 0.05° up to 102 °C , and between and For a discussion of accuracies attainable with such thermometers see National Bureau of Standards Circular 600, Calibration of Liquid-in-Glass Thermometers.

For the Director
James F. Swindells

Test No. 311-30-64
Completed: December 3, 1964
KSL:dh

James F. Swindells, Chief
Thermometry Laboratory
Heat Division

USCOMM-DC 18507-P63

FIGURE 1.—*Facsimile of face of a Report of Calibration.*

NOTES

*NOTE A.-The tabulated corrections apply for the condition of total immersion of the bulb and liquid column. If the thermometer is used at partial immersion, apply an emergent stem correction as explained in the accompanying stem correction sheet.

NOTE B.-The tabulated corrections apply for the condition of total immersion of the bulb and liquid column. Although this thermometer is not ordinarily used in this way, no significant errors should be introduced by neglecting the corrections for emergent stem.

NOTE C.-The thermometer was tested in a large, closed-top, electrically heated, liquid bath at an immersion of The temperature of the room was about 25° C (77° F). If the thermometer is used under conditions which would cause the average temperature of the emergent liquid column to differ markedly from that prevailing in the test, appreciable differences in the indications of the thermometer would result.

NOTE D.-The tabulated corrections apply provided the ice-point reading is If the ice-point reading is found to be higher (or lower) than stated, all other readings will be higher (or lower) by the same amount.

*NOTE E.-The tabulated corrections apply provided the ice-point reading, taken after exposure for not less than 3 days to a temperature of about 25° C (77° F) is −0.06 °C . If the ice-point reading is found to be higher (or lower) than stated, all other readings will be higher (or lower) by the same amount. If the thermometer is used at a given temperature shortly after being heated to a higher temperature, an error of 0.01° or less, for each 10° difference between the two temperatures, may be introduced. The tabulated corrections apply if the thermometer is used in its upright position; if used in a horizontal position, the indications may be a few hundredths of a degree higher.

NOTE F.-The tabulated corrections apply provided the reading when the thermometer is immersed in steam at 100° C (212° F) is If the reading is found to be higher (or lower) than stated, all other readings will be higher (or lower) by the same amount. The temperature of steam is 100° C (212° F) only if the pressure is 760 mm (29.921 inches). If the pressure differs from 760 mm (29.921 inches) allowance must be made for this. If the pressure is higher (or lower) than 760 mm (29.921 inches) the temperature will be higher (or lower) than 100° C (212° F) by approximately 0.037° C per mm difference (1.68° F per inch difference).

NOTE G.-The thermometer, before testing, was heated to the temperature of the highest test point. The application of the tabular corrections to the readings of the thermometer will give true temperature differences provided the thermometer is used in its upright position and is heated previously (within an hour before using) to the highest temperature to be measured.

NOTE H.-The thermometer was tested for use in differential measurements, such as the measurement of temperature differences in a flow calorimeter. The two thermometers used in a flow calorimeter should be compared occasionally in stirred water at some convenient temperature and if their indications, after application of the tabular corrections, are found to differ, an additional correction equal to the difference should be applied to the indications of one of them.

NOTE I.- The tabulated corrections apply for a "setting" of 20° C. Setting factors for use with other settings are given on the accompanying sheet.

NOTE J.-The tabulated corrections apply for the condition of immersion indicated provided the ice-point reading, taken after heating to for not less than 3 minutes, is If the ice-point reading, which should be taken within 5 minutes after removal of the thermometer from the heated bath, is found to be higher (or lower) than stated all other readings will be higher (or lower) by the same amount.

NOTE K.-At temperatures below the ice-point this thermometer was tested under conditions of total immersion of the bulb and liquid column. The stated corrections were computed using a value of K= /° and an assumed temperature of ° for the emergent stem.

Special Note.-

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FIGURE 2.—*Facsimile of back of a Report of Calibration.*

its judgment of the best method of shipping unless specific instructions are received. Such instructions should be supplied at the time that arrangements are being made for the test. If a test number has been assigned prior to the shipment, this number should appear on the shipping container. If a test number has not been assigned at this time, a purchase order, or letter should be sent under separate cover. In either case the shipment should include a packing list.

All possible care will be taken in handling thermometers at the Bureau, but the risk of damage either in shipment or in testing must be assumed by the applicant. The applicant should consider the nature of the equipment he is shipping and pack it accordingly, with appropriate labeling. Attention is called to the availability of security express in shipping thermometers.

3. Definitions

The principal features of a solid-stem liquid-in-glass thermometer are shown in figure 3. Not all of the features shown would necessarily be incorporated in any one thermometer.

Bulb: The liquid reservoir. The bulb of a thermometer will contain a volume equivalent to a specific number of degrees of the scale depending upon the coefficients of expansion of the thermometric liquid and bulb glass. For mercury in a "normal" glass bulb the volume is equivalent to about 6200 °C, or 11, 200 °F. For organic thermometric liquids with higher coefficients of expansion than mercury, the degree equivalents of the bulb volume are correspondingly lower.

Stem: The glass capillary tube through which the thermometric liquid advances or retreats with change in temperature.

Main Scale: The scale graduated in degrees or multiples or submultiples of degrees.

Auxiliary Scale: A short scale including a reference temperature such as the ice point, to provide a means for checking thermometer for change in calibration with time. (See sec. 7.4.) This scale is added when a suitable reference temperature is not included in the range of the main scale.

Expansion Chamber: An enlargement at the top end of the capillary bore having a volume equivalent to not less than 20 mm of unchanged capillary. Smaller chambers are not regarded as expansion chambers. The expansion chamber is provided to prevent the buildup of excessive pressures in gas-filled thermometers as the liquid filling advances toward the top of the scale.

Contraction Chamber: An enlargement of the capillary bore which serves to reduce a long length of capillary or to prevent contraction of the liquid column into the bulb. This chamber is introduced below the main scale or between the main scale and an auxiliary scale.

Reference Point: Some reference temperature, within the range of the main scale or an auxiliary scale, such as the ice point or steam point, at which the thermometer may be checked periodically for changes in scale calibration. (See sec. 7.4.)

Total Immersion Thermometer: A thermometer designed to indicate temperatures correctly when used with the bulb and the entire liquid column in the stem exposed to the temperature being measured.

Partial Immersion Thermometer: A thermometer designed to indicate temperatures correctly when used with the bulb and a specified part of the stem exposed to the temperature being measured. The remaining part of the stem will be at the ambient temperature, usually different from the temperature being measured. Such thermometers are marked with an *immersion line* to indicate the proper depth of immersion. The *emergent stem* refers to the length of liquid column and stem at the ambient temperature.

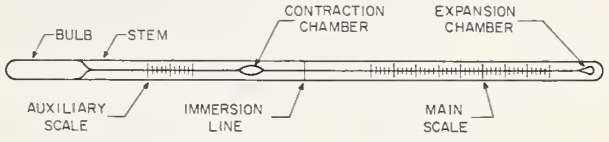

FIGURE 3.—*Principal features of a solid-stem liquid-in-glass thermometer.*

Complete Immersion Thermometer: A thermometer designed to indicate temperatures correctly when the whole thermometer, including the expansion chamber, is exposed to the temperature being measured. In gas-filled thermometers the reading will be different for complete, as compared to total immersion as a result of the effect of temperature on the gas pressure in the thermometer. (See sec. 8.2). The difference in readings under the two conditions is particularly significant at high temperatures.

Calibration Points are the temperatures at which corrections to the thermometer scale are determined.

Accuracy: The accuracy of a measurement refers to the closeness with which the result of the measurement approaches the true value of the quantity being measured. In this Monograph the accuracy expected of a given thermometer refers to the closeness of the observed indication of the thermometer to the true temperature on the International Practical Temperature Scale. The accuracy attainable is principally limited by the characteristics of the thermometer itself. Instability of the thermometer glass, capillary forces at the surface of the thermometric liquid, non-uniformity of capillary bore, and inaccuracies in scale graduation are among the important factors. With partial immersion thermometers, uncertainties in corrections for the emergent stem may greatly limit the accuracy. Observer errors are also involved, but with care these can usually be made relatively small.

Precision: The precision of measurement refers to the degree of agreement amongst repeated measurements of the same quantity. When a thermometer is held at constant temperature and it is read repeatedly at the same scale reading, one can be deceived in assuming that a corresponding accuracy is being achieved. For example, capillary forces may be holding the liquid column at the false level, or the bulb volume may have changed since the time of calibration.

4. Temperature Scales and Standards

The calibration of a thermometer consists of comparing its indications with known temperatures on a standard scale of temperature. By international agreement, the Kelvin Scale is now accepted as the absolute Thermodynamic scale. In 1954 the Tenth General Conference on Weights and Measures defined the Kelvin Scale by means of a single fixed point, the triple point of water, to which was assigned the temperature 273.16 °K, exactly. Because of the difficulties encountered in the practical realization of the Kelvin Scale, however, a practical working scale, the International Temperature Scale, was first adopted in 1927 and later revised in 1948. In 1960 the Eleventh General Conference changed the name of the scale to International Practical Temperature Scale of 1948 (IPTS) and adopted a revised text of the scale [2]. The Scale itself was not changed, however. The new text, therefore, does not change the value of any temperature on the 1948 scale by as much as the experimental error of measurement. This Scale is intended to have close correspondence with the Kelvin Scale and to provide scientific and industrial laboratories throughout the world with a common basis for stating temperatures. Calibrations of thermometers at the Bureau, therefore, are made with reference to temperatures on the IPTS.

In the range of temperatures normally covered by liquid-in-glass thermometry, the IPTS is defined by four fixed points, the normal boiling point of oxygen at −182.97 °C, the triple point of water at +0.01 °C, the normal boiling point of water at 100 °C, and the normal boiling point of sulfur at 444.6 °C. In place of the sulfur point, however, the text of the Scale recommends the use of the temperature of equilibrium between solid zinc and liquid zinc (zinc point) with the value of 419.505 °C. Experience has shown the zinc point to be more reproducible than the sulfur point. Temperatures in the range −182.97 to 630.5 °C, at other than these fixed points, are defined in terms of a standard platinum resistance thermometer calibrated at the four fixed points and using a specified equation for interpolation.

Temperatures on the IPTS are expressed in degrees Celsius (centigrade). Thermometers graduated on the Fahrenheit Scale are calibrated with reference to the IPTS using the conversion formula,

$$\text{temperature in °F} = \frac{9}{5}\,(\text{temperature in °C}) + 32.$$

When the highest accuracy is required in a calibration, the thermometer indications are compared directly with temperatures obtained with a standard resistance thermometer. If lesser accuracy is adequate, one of a series of mercury-in-glass standards is used, except below 0 °C and above 300 °C, where the calibration is made directly with a resistance thermometer regardless of the accuracy required. The series of mercury-in-glass thermometers which serve as standards for total-immersion comparisons is shown below.

Range	Smallest graduation	Auxiliary scale
°C	°C	°C
0 to 50	0.1	
0 to 100	0.2	
50 to 100	0.1	at 0
100 to 200	0.2	at 0
200 to 300	0.5	at 0

These standards are calibrated with reference to the IPTS through comparisons with a standard resistance thermometer.

Partial-immersion standards, known as "like standards", are maintained for the calibration of accepted designs of partial-immersion thermometers. These standards are calibrated for stem-temperature conditions expected to prevail during the calibration of similar thermometers. This use of like standards eliminates the need for many of the precautions necessary when dissimilar thermometers are compared. The procedure permits the direct comparison of the indications of similar thermometers as long as the bulbs are at the same temperature and the stem temperatures are essentially the same for all of the thermometers under comparison.

For those who may want to use reproducible fixed points in their own laboratories, the Bureau sells triple-point-of-benzoic-acid cells, 122 °C (252 °F); and freezing point cells of phenol, 41 °C (106 °F), naphthalene, 80 °C (176 °F), and phthalic anhydride, 131 °C (268 °F). At higher temperatures freezing point standards of tin, 232 °C (450 °F); lead, 327 °C (621 °F); and zinc, 419 °C (786 °F) are available. (All of the above temperatures are approximate, but precise values are supplied with the standards.) Detailed information on these cells and standards and their procurement is given in NBS Miscellaneous Publication 241.

5. Calibration Procedures

All liquid-in-glass thermometers are calibrated in terms of the IPTS as defined by the standard platinum resistance thermometer. The readings may be compared directly with a standard resistance thermometer, or indirectly using a mercury-in-glass standard. Ice and steam baths, together with a series of stirred liquid baths, provide controlled temperature media for the comparisons.

5.1. Equipment

a. Ice Bath

Through the use of an ice bath, the ice point may be realized conveniently to better than 0.01 °C. A Dewar flask serves as a container for the ice, the melting of the ice being retarded by the insulating properties of the vessel. Ice shaved from clear cakes is mixed with distilled water to form a slush. Enough water is used to afford good contact with the thermometers, but not so much as to float the ice. From time to time excess water is syphoned from the bath. Care is taken to prevent contamination of the ice and water. A small reading telescope with a magnification of 10 diameters aids in reading the thermometer indication and reduces parallax errors. Gently tapping the thermometer just before reading may prevent the sticking of a falling meniscus. On the other hand too vigorous a tap will occasionally cause the mercury to rebound to an erroneously high reading.

b. Steam Bath

The steam point may be realized in a steam-point apparatus either by comparing the thermometers with standards or by the determination of the temperature of the steam from a measurement of the prevailing atmospheric pressure.

The steam bath, shown in figure 4, consists of a double-walled steam jacket in which steam from a boiler circulates. The thermometers are suspended in such a manner as to insure free circulation of steam around them. Provision is made for either relieving any excess pressure in the space surrounding the thermometers, or for determining the excess by means of a small differential manometer.

When the steam bath is used as a fixed-point apparatus a barometer is a necessary accessory since the true temperature of the steam is dependent upon the prevailing atmospheric pressure. The usual corrections are applied to the barometer reading including any corrections necessary for the value of local acceleration of gravity, for the difference in height of the steam bath and the barometer, and for any excess pressure above atmospheric in the steam jacket. The steam temperature may then be found from the pressure-temperature values given in table 1. With a good barometer, accurate to 0.1 mm Hg, this procedure is capable of an accuracy of 0.002 to 0.003 deg C (0.004 to 0.005 deg F). The Fortin type barometer will usually serve for all but the most exacting measurements.

The steam bath is also used as comparison bath, in which case the temperature of the steam is determined at the time of test by means of a previously standardized thermometer. This method is simpler than determining the steam temperature from a barometer reading, and may be preferable, particularly when a resistance thermometer can be used as the standard.

c. Comparison Liquid Baths

Stirred liquid baths of two designs are used at the Bureau as comparators in which thermometers are calibrated in the range −40 to +500 °C. (−40 to +930 °F). This equipment permits stirring adequate for uniform temperature distribution, and provides controlled heat input for temperature regulation.

A type suitable for use with media liquid at room temperature is shown in figure 5. This bath is constructed with two tubes of different diameters having connecting passages at the top and bottom. The heating coil, cooling coil for circulating cold water for comparisons below room

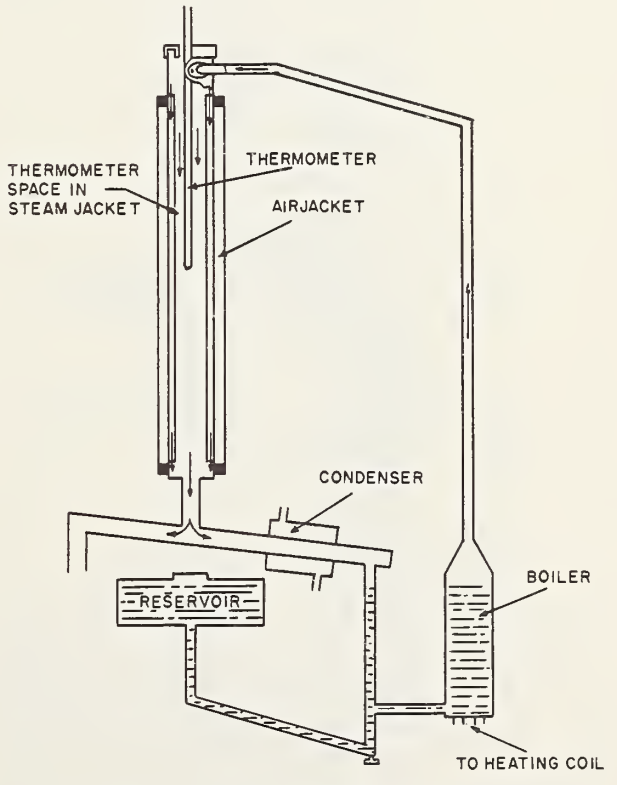

FIGURE 4.—*Schematic drawing of steam bath.*

TABLE 1.—*(Thermometric) condensation temperature of steam [3]*

[Astrisk (*) indicates change in integer]

P	Pressure in mm mercury (standard)									
	0	1	2	3	4	5	6	7	8	9
	Temperature in degrees of International Scale									
500	88.678	0.730	0.782	0.834	0.886	0.938	0.990	*0.042	*0.093	*0.144
510	89.196	.247	.298	.350	.401	.452	.502	.553	.604	.655
520	0.705	.756	.806	.856	.907	.957	*.007	*.057	*.107	*.157
530	90.206	.256	.306	.355	.405	.454	.503	.553	.602	.651
540	0.700	.749	.798	.846	.895	.944	.992	*.041	*.089	*.138
550	91.186	.234	.282	.330	.378	.426	.474	.521	.569	.617
560	0.664	.712	.759	.806	.854	.901	.948	.995	*.042	*.089
570	92.136	.182	.229	.276	.322	.369	.415	.462	.508	.554
580	0.600	.646	.692	.738	.784	.830	.876	.922	.967	*.013
590	93.058	.104	.149	.195	.240	.285	.330	.375	.420	.465
600	0.5100	.5548	.5996	.6443	.6889	.7335	.7780	.8224	.8668	.9112
610	.9554	.9996	*.0438	*.0879	*.1319	*.1759	*.2198	*.2636	*.3074	*.3511
620	94.3948	.4384	.4820	.5255	.5689	.6123	.6556	.6989	.7421	.7852
630	0.8283	.8713	.9143	.9572	*.0001	*.0429	*.0857	*.1284	*.1710	*.2136
640	95.2562	.2987	.3411	.3834	.4257	.4680	.5102	.5523	.5944	.6365
650	95.6785	.7204	.7623	.8041	.8459	.8876	.9293	.9709	*.0125	*.0539
660	96.0954	.1368	.1782	.2195	.2607	.3019	.3431	.3842	.4252	.4662
670	0.5072	.5480	.5889	.6297	.6704	.7111	.7517	.7923	.8329	.8734
680	.9138	.9542	.9946	*.0349	*.0751	*.1153	*.1555	*.1956	*.2356	*.2756
690	97.3156	.3555	.3954	.4352	.4749	.5146	.5543	.5939	.6335	.6730
700	0.7125	.7519	.7913	.8307	.8700	.9092	.9484	.9876	*.0267	*.0657
710	98.1048	.1437	.1827	.2216	.2604	.2992	.3379	.3766	.4153	.4539
720	0.4925	.5310	.5695	.6079	.6463	.6846	.7229	.7612	.7994	.8376
730	.8757	.9138	.9519	.9899	*.0278	*.0657	*.1036	*.1414	*.1792	*.2110
740	99.2547	.2924	.3300	.3675	.4051	.4426	.4800	.5174	.5548	.5921
750	0.6294	.6667	.7039	.7410	.7781	.8152	.8523	.8893	.9262	.9631
760	100.0000	.0368	.0736	.1104	.1471	.1838	.2204	.2570	.2936	.3301
770	0.3666	.4030	.4394	.4758	.5121	.5484	.5846	.6208	.6570	.6932
780	.7293	.7653	.8013	.8373	.8733	.9092	.9450	.9808	*.0166	*.0524
790	101.0881	.1238	.1594	.1950	.2306	.2661	.3016	.3371	.3725	.4079

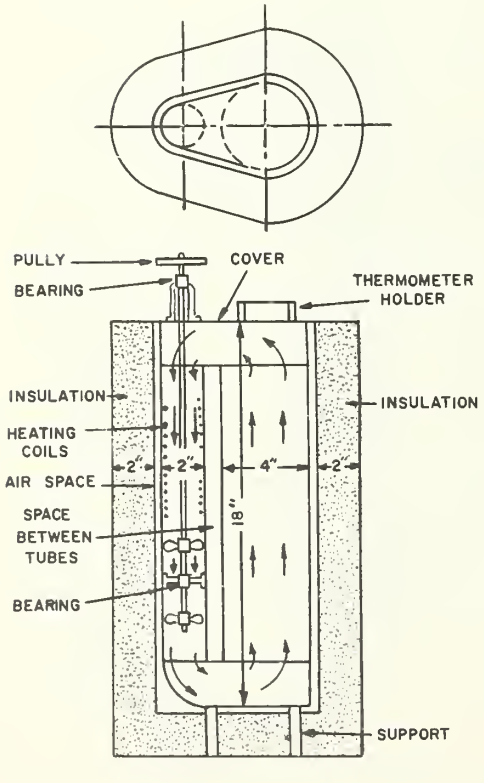

FIGURE 5.—*Stirred liquid bath.*

temperature, and stirrer are located in the smaller tube, the larger tube being left clear for immersion of the thermometers.

The type shown in figure 6 is designed for use at high temperatures with molten tin as the bath liquid. The bath is made with two coaxial tubes of which the inner tube is open at both ends. The stirring propeller is mounted near the bottom of the inner tube leaving the space above the propeller free to receive thermometers which are inserted in reentrant tubes. Heat is supplied by heater coils wound on the outside tube. As is also the case with the bath shown in figure 5, the thermometers are shielded from direct radiation from the hotter parts of the bath.

In each type of bath a 2- or 3-in. thickness of insulation reduces heat loss and thus aids in maintaining a uniform temperature distribution throughout the bath liquid. Each bath is provided with an insulated cover carrying a thermometer holder which can be rotated to bring successive thermometers into the field of a vertically adjustable reading telescope.

For calibrations in the range 5 to 99 °C (40 to 210 °F) water is used as the bath liquid. One grade of petroleum oil is used between 99 and 200 °C (210 and 392 °F) and a second between 200 and 315 °C (392 and 599 °F). The oils are chosen with properties such that they are not too viscous for adequate stirring at the lower temperature but at the same time have flash points which

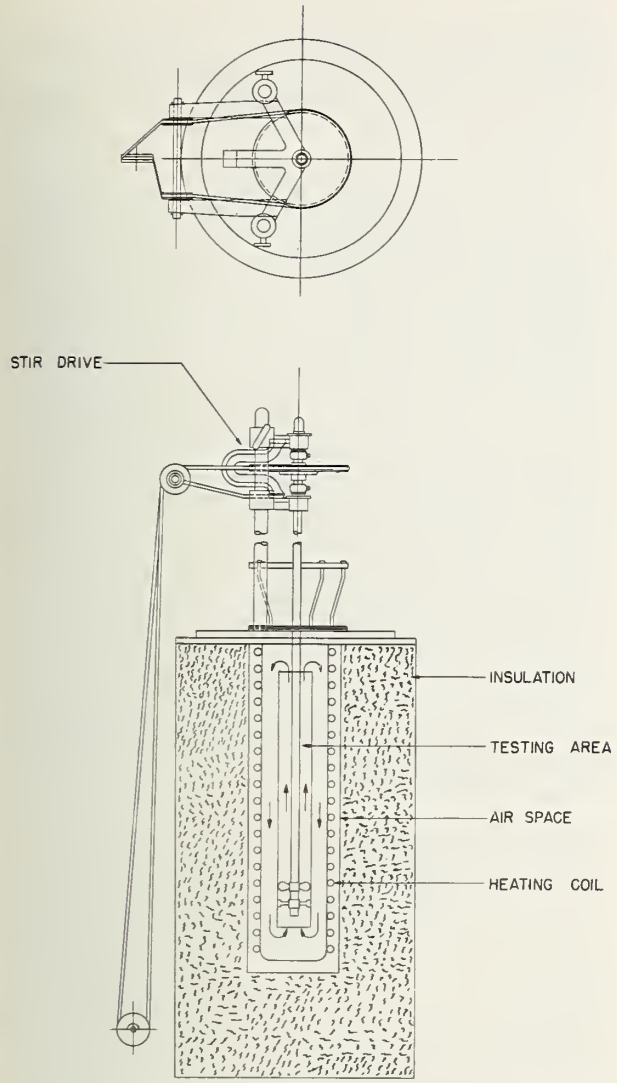

FIGURE 6.—*Stirred high-temperature bath using liquid having freezing point above room temperature.*

are not exceeded at the higher temperatures. The tin bath is used from 315 °C up to about 540 °C (599 to 1004 °F).

Calibrations from 0 to −110 °C (32 to −166 °F) are made in a cryostat similar in essentials to that described by Scott and Brickwedde [4]. The cryostat, shown in figure 7, consists of an inner Dewar flask, D, which contains the bath liquid, surrounded by liquid nitrogen in the outer Dewar flask, C. The rate of heat transfer between the bath liquid and the liquid nitrogen is controlled by varying the gas pressure between the walls of the inner Dewar flask, which is connected to a vacuum system through the side tube, M. Vigorous stirring of the bath liquid is maintained by the propeller, I, which circulates liquid upwards through the inside of the stirrer tube, P, and down the outside. Excess refrigeration is compensated by thermostatically controlled heat supplied by a heater coil, J, wound outside the stirrer tube.

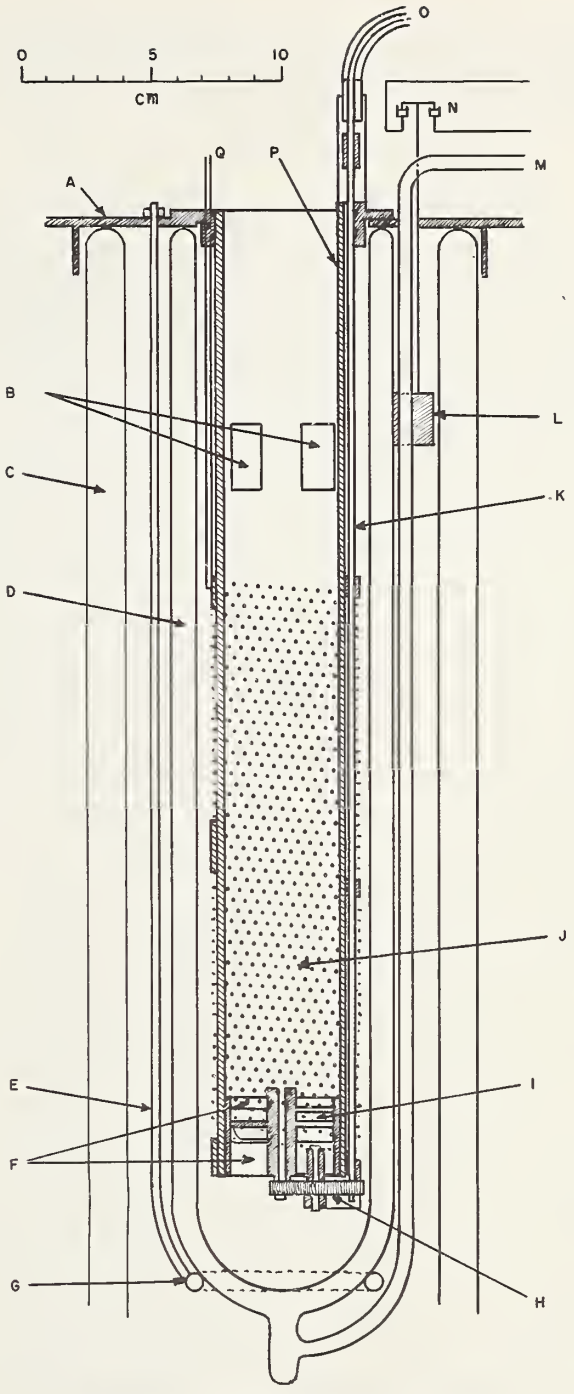

FIGURE 7.—*Vertical section of cryostat.*

For temperatures down to −75 °C (−103 °F) the bath liquid used is the eutectic mixture of carbon tetrachloride and chloroform (49.4 percent, by weight, of CCl_4, and 50 6 percent of $CHCl_3$), which freezes at about −81 °C (−114 °F). For temperatures between −75 and −110 °C (−103 and −166 °F) a five-component mixture is used containing 14.5 percent of chloroform, 25.3 percent of methylene chloride, 33.4 percent of ethyl

bromide, 10.4 percent of transdichloroethylene, and 16.4 percent of trichloroethylene. This mixture freezes at about −150 °C (238 °F), but absorbs moisture readily and becomes cloudy at somewhat higher temperatures.

5.2. Number and Choice of Test Points

Usually corrections to a thermometer scale are measured at uniformly spaced calibration points covering the whole range of the main scale. The length of scale between calibration points should be chosen with regard to the accuracy expected of the thermometer in use. The points should not be chosen unnecessarily close together, nor should they be spaced so far apart as to destroy confidence in interpolated corrections at temperatures between the calibration points. For many years the predecessors of this Monograph have contained the statement: "In general, if the readings of a thermometer are to be trusted to one or two-tenths of the smallest scale division, the interval between test points should not exceed 100 divisions and usually need not be less than 40." Recent studies of calibration data for over 50 thermometers purchased during the years 1930 through 1956 for use as laboratory standards showed that, while there was considerable variation between individual thermometers, the above statement was usually applicable only to thermometers not graduated above about 200 °C. For the thermometers not graduated above 200 °C, calibrations every 40 to 50 divisions were required for interpolation to one or two-tenths of a division. In nearly all cases, interpolation between calibrations 100 divisions apart could be relied upon only to one-half of a division. For most of the thermometers graduated above 200 °C, the data showed that interpolations between calibrations 40 to 50 divisions apart were reliable to only one-half division, and that the spacing had to be reduced to 20 to 25 divisions if interpolation to one or two-tenths division was to be expected. It was found also that an examination of scale corrections obtained a given number of divisions apart for a particular thermometer was not sufficient to predict whether or not more calibration points were required for reliable interpolation. The above studies were made with only a few of the many types of thermometers submitted to the Bureau for calibration, and, therefore, conclusions may not necessarily be applicable to other types. Experience with a particular type of thermometer seems to be the most reliable guide in the choice of calibration points.

When a thermometer is to be calibrated without reference to any special use, the choice of calibration points should be left to the calibration laboratory. In some cases the number and distribution of test points can be decided only after a careful inspection of the thermometer. If the thermometer is to be used for a special purpose, this fact should be clearly stated before calibration. The Bureau will not make calibrations at more, or fewer, points than are necessary, although this judgment may be influenced by considerations given to special requests. In any case, no fewer than two points are taken on the main scale. At least one reference point is included as a calibration point when such a point (or points) is included in the scale.

5.3. Determination of Scale Corrections

Through considerations of accuracy, Beckmann thermometers, calorimeter thermometers, and thermometers graduated in tenths of a degree Fahrenheit are calibrated using a platinum resistance thermometer. A platinum thermometer is also used for all calibrations made below 0 °C (32 °F) or above 300 °C (572 °F). Other calibrations are generally made using mercury-in-glass standards (listed in sec. 4) which have been calibrated with a platinum thermometer.

When comparing thermometers with liquid-in-glass standards two standards are always used. In this way reading errors are more readily detected and cross checks of the standards are maintained. The comparison procedures are described in simplified form in the following hypothetical test of four thermometers, T1 through T4.

Table 2 shows the observations taken in obtaining the corrections applicable to the thermometers at 20 °C. For simplification, all of the entries in the table reflect perfect thermometer performance and no observer error.

TABLE 2.—*Comparison of test thermometers with liquid-in-glass standards*

	S1	T1	T2	T3	T4	S2
Ice-point readings of test thermometers						
Observer A	-------	+0.02	−0.02	+0.02	0.00	-------
Observer B	-------	+.02	−.02	+.02	0.00	-------
Mean ice points	-------	+.02	−.02	+.02	.00	-------
Thermometer comparisons						
Observer A reading left to right	19.87	19.98	19.96	20.02	20.03	19.89
Observer A reading right to left	19.88	19.99	19.97	20.03	20.04	19.89
Observer B reading left to right	19.88	19.99	19.97	20.04	20.05	19.90
Observer B reading right to left	19.89	20.00	19.98	20.04	20.05	19.90
Means	19.88	19.99	19.97	20.03	20.04	19.89_5
Ice-point readings of standards						
Observer A	−0.01	-------	-------	-------	-------	−0.08
Observer B	−.01	-------	-------	-------	-------	−.08
Mean ice points	−.01	-------	-------	-------	-------	−.08
Calculations of corrections						
Correction to standards	+0.12	-------	-------	-------	-------	+0.04
Mean temperature, each standard	20.01	-------	-------	-------	-------	20.01_5
Mean temperature of all readings	-------	-------	20.01	-------	-------	-------
Corrections to test thermometers	-------	+0.02	+0.04	−0.02	−0.03	-------

The first observations are the ice points of the thermometers under test. These are entered in the upper part of the table. The thermometers are then mounted in the comparison bath between the two standards, and the power to the bath is so

adjusted that its temperature is slowly increasing at a steady rate. The data shown in the table are for a temperature rise of 0.001° between each observation. Two observers (A and B) are used, first with one observer reading and the other recording, and next with the observers interchanged. Observer A reads in the order left to right as the thermometers appear in the table and then repeats the observations in the order right to left. Observer B then immediately reads in the same manner. The observations are spaced uniformly in time so that, with the bath temperature increasing linearly with time, the mean of the observations with any one thermometer will correspond to the mean temperature of the comparison bath during the observations of all of the thermometers. Immediately after the comparison observations, ice points are taken of the two standards. Using these ice point data, together with the known scale corrections for the standards, the temperatures indicated by the standards are calculated and an overall mean temperature for the observations is obtained. This overall mean temperature is compared with the mean of the observations for each thermometer to obtain a correction to the scale of the thermometer at this point. The thermometer comparisons are then repeated at the next higher test point and so on until corrections are obtained at a sufficient number of points to calibrate the complete scale, as specified in section 5.2.

When a resistance thermometer standard is used, the sequence of observations is the same except that only one standard is used, the same resistance thermometer being read four times in place of the separate observations of two liquid-in-glass standards.

Ice-point readings are not usually taken with each test point on the scale. For thermometers not graduated above 300 °C or 600 °F, ice points taken before the first test point on the scale and after the last point will usually suffice. With high-temperature thermometers, however, it is the practice to take an ice point and then test immediately at the highest test point on the scale. After a rest period of 3 days at room temperature a second ice point is taken. If a change in ice point is found that is greater than the expected accuracy of the thermometer, the thermometer is deemed unsuitable for calibration and further tests are unnecessary.

The corrections obtained in this manner apply as long as the ice point remains the same as that observed during calibration. Subsequent changes in the ice point will be a result of small changes in the glass which affect the volume of the thermometer bulb. The volume of the capillary stem also changes, but the volume of mercury contained in the stem is so small in comparison to that in the bulb that changes in the stem volume can usually be ignored. As a result, changes in the ice-point reading will be duplicated by similar changes in readings at each point along the scale. Thus, when during use the correction at the ice point is found to be higher (or lower) than that observed at the time of calibration, the other reported corrections to the scale can confidently be taken to be higher (or lower) by the same amount.

5.4. Corrections for Emergent Stem

The proper application of scale corrections as reported in NBS Reports presents no difficulties in cases where thermometers are calibrated and used under conditions of total immersion. In such cases the temperature of the thermometer, including the stem up to the top of the mercury thread, is definitely specified and the corrections as given apply when the thermometer is used at total immersion. Instances frequently occur, however, where some part of the mercury column is emergent from the region whose temperature is being measured. In these cases the emergent part of the stem may be in an environment, not only in which the temperature is markedly different from that of the thermometer bulb, but in which pronounced temperature gradients may be present. If such a situation exists in the use of a thermometer which has been calibrated at total immersion, a correction may be calculated to account for the difference in temperature between the bulb and the emergent stem. The calculation of this correction requires a reliable estimate of the mean temperature of the emergent stem, which, for the best work, will be made from measurements. But if the stem temperature measurements are not repeated each time the thermometer is used, the accuracy of the correction will depend upon the constancy of the stem temperature over periods of time. For example, if the emergent stem is exposed to the air above a liquid bath, variations in ambient temperature and air circulation can cause significant variations in the temperature of the emergent stem.

The same situation occurs in the case of partial-immersion thermometers. For this type of thermometer, the reported scale corrections apply only for the indicated depth of immersion and a particular stem temperature. If the thermometer is then used under conditions where the mean stem temperature is different, the reported scale corrections are not applicable, and a stem temperature correction is required.

The following paragraphs describe methods for determining stem temperatures and calculating corrections. For a known or assumed condition, the use of these formulas will indicate the importance of the stem correction in relation to a desired accuracy, and the corrections can then be applied as necessary.

a. Measurement of Emergent-Stem Temperature

The mean temperature of the emergent stem may be measured approximately by means of one or more small auxiliary thermometers suspended near the emergent stem, or more accurately by

exposing a similar stem and capillary mercury column beside the emergent stem and thus measuring its mean temperature [5, 6]. This is conveniently carried out with a faden thermometer ("thread thermometer") in which the expansion of the mercury in a capillary tube (bulb) is measured in a still finer capillary stem.

The methods used at the NBS in calibration work are based upon the use of faden thermometers whenever possible. These thermometers have very long bulbs (5 to 20 cm) with wall thicknesses and bore sizes nearly the same as the stem of an ordinary thermometer. If a faden thermometer is placed beside a thermometer to be observed, at such a height that the top of the faden thermometer bulb is at the same level as the top of the mercury column in the thermometer, the faden thermometer reading will give approximately the mean temperature of the adjacent portion of the thermometer stem and mercury thread. For example, a faden thermometer with a 10-cm bulb will give the mean temperature of the adjacent 10 cm of the thermometer stem. This method of using the faden thermometer is convenient for correcting the readings of a total-immersion thermometer when being used at partial immersion. The use of a faden thermometer in this manner is illustrated in figure 8(a) for the case where the mercury column in a total immersion thermometer extends a short distance above the surface of the bath to permit reading. In this case a correction must be calculated for the emergent part of the mercury column. If the stem temperature of a partial-immersion thermometer is to be measured, one or more faden thermometers are mounted so as to indicate the mean stem temperature between the immersion mark and the top of the mercury column, as shown in figure 8(b). If faden thermometers are not available, an estimate of the stem temperature can be made with auxiliary thermometers as in figure 8(c).

In calculating the correction for the emergent stem, it is convenient to express the length of thermometer stem adjacent to the faden bulb in terms of degrees on the thermometer scale. Thus, for a 10-cm faden thermometer, the number of degrees corresponding to 10 cm must be found by measurement of a portion of the thermometer scale. This measurement should be made over the portion of the graduated scale which was adjacent to the faden bulb. This is particularly important with high-temperature thermometers where the length of a degree is generally not the same at all parts of the scale.

b. Formula for Total-Immersion Thermometers

When a thermometer, which has been graduated and calibrated for use at total immersion is actually used at partial immersion, the correction for the emergent stem may be calculated by the general formula,

$$\text{stem correction} = Kn\ (T-t),$$

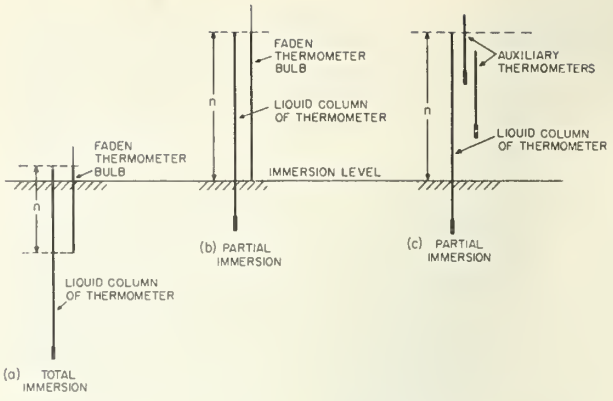

FIGURE 8.—*Schemes for measurement of emergent stem temperature.*

where

K = differential expansion coefficient of mercury (or other thermometric liquid) in the particular kind of glass which the thermometer is made (see table 3),

n = number of thermometer scale degrees adjacent to the faden thermometer,

t = average temperature of n degrees of the thermometer stem (faden thermometer reading),

T = temperature of the thermometer bulb.

The coefficient K is different for different kinds of glass, and even for the same glass, it differs for different temperature intervals, i.e., different values of $(T-t)$. Since most of the change results from the varying coefficient of the mercury, the change in K with temperature for one glass may reasonably be inferred from the change for another glass.

Calculation of the stem correction may be illustrated by the following example:

A total-immersion thermometer reads 90° C in a bath when immersed to the 80 °C graduation mark on the scale, and a 10-cm faden thermometer

TABLE 3.—*Values of* K *for mercury-in-glass thermometers*

Mean temp. $\frac{T°+t°}{2}$	K for "normal" glass	K for "borosilicate" glass
For Celsius thermometers		
0°	0.000158	0.000164
100	.000158	.000164
150	.000158	.000165
200	.000159	.000167
250	.000161	.000170
300	.000164	.000174
350	--------	.000178
400	--------	.000183
450	--------	.000188
For Fahrenheit thermometers		
0°	0.000088	0.000091
200	.000088	.000091
300	.000088	.000092
400	.000089	.000093
500	.000090	.000095
600	.000092	.000097
700	--------	.000100
800	--------	.000103

placed alongside the thermometer is adjacent to the scale between 60 and 90 °C. For this case $n=90-60=30$. If the faden thermometer indicates 80 °C, then the stem correction $=0.00016\times 30(90-80)=+0.048$, or $+0.05$ °C. Note that when the temperature of the emergent stem is lower than the bath temperature, the sign of the correction is +.

If a faden thermometer were not available in the above example, the emergent-stem temperature could be estimated by suspending a small auxiliary thermometer above the bath adjacent to the main thermometer and with its bulb centered at about the level of the 85° graduation. The reading of the auxiliary thermometer will then approximate the mean temperature of the 10 deg C (80° to 90 °C) emergent from the bath. For this condition $n=10$. If the auxiliary thermometre reads 60 °C, the stem correction $=0.00016\times 10(90-60)=+0.048$ or $+0.05$ °C. This method will usually not be as reliable as the method using a faden thermometer [6].

c. Formula for Partial-Immersion Thermometers

The scale corrections for partial-immersion thermometers calibrated at the Bureau are reported for the conditions of immersion to the depth of the immersion mark on the thermometer and, unless otherwise requested, for the unspecified stem temperatures resulting from the particular environments prevailing over the comparison baths in the course of the calibration. Frequently, however, thermometers are submitted for calibration with a request for scale corrections which are applicable to a specified mean temperature of the emergent stem. In such cases the emergent stem temperatures are measured during the process of calibration. The calibration observations are then corrected as necessary to account for any differences found between the stem temperatures observed during test and the specified stem temperature for which the scale corrections are to apply. In this case, the magnitude of the stem correction is proportional to the difference between the specified and observed stem temperatures and may be calculated for Celsius mercurial thermometers by means of the relation,

$$\text{stem correction}=0.00016n(t_{sp}-t_{obs}),$$

where

t_{sp} = specified mean temperature of emergent stem (for which reported scale corrections apply),
t_{obs} = observed mean temperature of emergent stem,
n = number of scale degrees equivalent to the length of emergent stem.

The above relation, of course, may also be used to correct the indications of a partial-immersion thermometer when used under stem-temperature conditions other than specified ones for which the scale corrections apply. In using the formula it should be noted that n applies to the whole length of emergent stem, i.e., from the immersion mark to the top of the mercury column. The ungraduated length between the immersion mark and the first graduation on the scale must therefore be evaluated in terms of scale degrees and included in the value of n.

For purposes of computing the emergent-stem correction, the value of K may be considered as depending on the average of T and t, that is $(T+t)/2$. Values of K as a function of $(T+t)/2$ for two widely used thermometer glasses are given in table 3. If the kind of glass is not known, K may be taken as 0.00016 for Celsius mercury thermometers and 0.00009 for Fahrenheit thermometers.

d. Formula for Calorimeter Thermometers

The stem correction is often important when thermometers are used for differential temperature measurements, as in calorimetry. In this case, provided the mean temperature of the stem remains constant, the correction may be computed from the following formula, involving the difference of the initial and final readings:

$$\text{stem correction}=Kd(T_1+T_2-S-t),$$

where

K = factor for relative expansion of glass and mercury,
T_1 and T_2 = the initial and final readings, respectively,
$d=T_2-T_1$,
S = scale reading to which the thermometer is immersed,
and t = mean temperature of the emergent stem.

This correction must be applied (added if +, subtracted if −) to the difference of the readings to give the true difference of temperature.

Example: Suppose the thermometer was immersed to its 20° mark; its initial reading, T_1, was 25 °C; its final reading, T_2, was 30 °C; and the stem temperature was 20 °C. Then the correction is $0.00016\times 5\ (25+30-20-20)=+0.012$ °C. The difference between T_1 and T_2 is 5°. The true difference between the initial and final temperatures was $T_2-T_1+\text{correction}=5.012$ °C.

e. Formula for Beckmann Thermometers

For a Beckmann thermometer the correction may be readily computed from the following formula, differing only slightly from that for calorimeter thermometers, provided the thermometer is immersed to near the zero on its scale and that the temperature of the stem remains constant:

$$\text{stem correction}=Kd(S+T_1+T_2-t),$$

where

S=setting of the thermometer (sec. 6.4), and the other symbols have the same meanings as for calorimeter thermometers.

A Beckmann thermometer of the ordinary type should not be used with any part of the lower portion of the stem exposed, as this part may contain 5 to 10 times as much mercury per centimeter as the graduated portion and, if exposed, introduces a large and uncertain error. If it is unavoidable, however, to use such a thermometer with some of the lower portion of the stem emergent from the bath, the necessary correction may be computed from the above formula, provided S in the formula is replaced by $S+m$, where m is the number of degrees the temperature of the thermometer must be lowered to bring the meniscus from the zero mark on its scale to the point of immersion.

If the thermometer is immersed to some point other than its zero mark, as would ordinarily be the case with thermometers having the zero graduation at the top of the scale, the differential stem correction may be calculated from the above formula if S is replaced by $S+m$. The formula is applicable whether the point of immersion is on the scale or below it, provided the points at which readings are made are above the point to which the thermometer is immersed.

6. Common Thermometers and Factors Affecting Their Use

In this section common types of high-grade thermometers are mentioned with a discussion of some of the factors affecting their use.

Tolerances allowed by the Bureau in issuing Reports of Calibration are given in tables 4 through 11 for individual types of thermometers. The values of these tolerances are the same as those given in the first edition of Circular 600 (1959). The accuracy bounds shown in the tables may seem broad in some instances, but the definite limitations of liquid-in-glass thermometry become apparent when all factors are considered. For example, if one keeps expanding the scale for more precise reading by reducing the capillary-bore diameter, a practical limit is reached beyond which capillary forces, in combination with the elasticity of the thermometer bulb, will prevent a smooth advance or retreat of the mercury column. Particularly with a slowly falling temperature, the movement of the mercury meniscus may be found to occur erratically in steps appreciably large in comparison to the graduation interval. Large "meniscus jumps" are associated with less rigid bulbs (relatively large diameters and/or thin walls) as well as small capillary-bore diameters. Excessively elliptical or flattened bores are not recommended. Thus increasing the length of a degree on the scale, for practical bulb sizes, improves thermometric performance to a certain point only, beyond which the precision of reading may readily be mistaken for accuracy in temperature measurement. A study of the effects of bulb and capillary dimensions on thermometer performance, made by Hall and Leaver [7], provides valuable guidelines for design purposes.

Other factors such as ice-point changes, unless exactly accounted for, and differences in external pressure may also account for inaccuracies much greater than the imprecision with which a scale having 0.1- or 0.2-deg graduations may be read.

6.1. Total-Immersion Thermometers

Thermometers pointed and graduated by the manufacturer to read correct temperatures when the bulb and entire liquid column in the stem are exposed to the temperature to be measured are known as "total-immersion" thermometers. While these thermometers are designed for immersion of all the mercury, it is not necessary, and in some cases not desirable, that the portion of the stem above the meniscus be immersed. The heating of this portion to high temperatures might cause excessive gas pressures resulting in erroneous readings if not permanent damage to the bulb.

In practice a short length of the mercury column often must be left emergent from the bath (or region) so that the meniscus will be visible when the temperature is being measured. If a large enough temperature difference exists between the bath and its surroundings, an appreciable temperature gradient may be found in the thermometer stem near the surface of the bath for which a correction to the thermometer reading may be required. The condition becomes more serious when a thermometer designed and calibrated for total immersion is intentionally used at partial immersion, that is with a significant portion of the liquid column at a temperature different from that of the bath. The reading will be too low or too high depending upon whether the surrounding temperature is lower or higher than that of the bath. For a total-immersion thermometer so used, an emergent stem correction must be determined and applied in addition to the calibration corrections. The correction may be as large as 20 Celsius degrees (36 Fahrenheit degrees) if the length of emergent liquid column and the difference in temperature between the bath and the space above it are large.

A method for determining this correction is given in section 5.4.b.

The scale tolerances shown in tables 4 and 5 are chosen to be indicative of good manufacturing practice. These tolerances are based on the fact that in the manufacture of thermometers certain small errors in pointing and graduation are inevitable, and also that the indications of thermometers are subject to variations due to the inherent properties of the glass. The tolerances

TABLE 4.—*Tolerances for Celsius total-immersion mercury thermometers*

Temperature range in degrees	Graduation interval in degrees	Tolerance in degrees	Accuracy in degrees	Corrections stated to
Thermometer graduated under 150 °C				
°C				
0 up to 150	1.0 or 0.5	0.5	0.1 to 0.2	0.1
0 up to 150	.2	.4	.02 to .05	.02
0 up to 100	.1	.3	.01 to .03	.01
Thermometers graduated under 300 °C				
0 up to 100	1.0 or 0.5	0.5	0.1 to 0.2	0.1
Above 100 up to 300		1.0	.2 to .3	.1
0 up to 100	.2	0.4	.02 to .05	.02
Above 100 up to 200		.5	.05 to .1	.02
Thermometers graduated above 300 °C				
0 up to 300	2.0	2.0	0.2 to 0.5	0.2
Above 300 up to 500		4.0	.5 to 1.0	.2
0 up to 300	1.0 or 0.5	2.0	.1 to 0.5	.1
Above 300 up to 500		4.0	.2 to .5	.1

TABLE 5.—*Tolerances for Fahrenheit total-immersion mercury thermometers*

Temperature range in degrees	Graduation interval in degrees	Tolerance in degrees	Accuracy in degrees	Corrections stated to
Thermometers graduated under 300 °F				
32 up to 300	2.0	1.0	0.2 to 0.5	0.2
32 up to 300	1.0 or 0.5	1.0	.1 to .2	.1
32 up to 212	.2 or .1	0.5	.02 to .05	.02
Thermometers graduated under 600 °F				
32 up to 212	2 or 1	1.0	0.2 to 0.5	0.2
Above 212 up to 600		2.0	.5	.2
Thermometers graduated above 600 °F				
32 up to 600	5	4.0	0.5 to 1.0	0.5
Above 600 up to 950		7.0	1. to 2.0	.5
32 up to 600	2 or 1	3.0	0.2 to 1.0	.2
Above 600 up to 950		6.0	.5 to 1.0	.2

must be sufficiently restrictive to insure to the user a satisfactory high-grade thermometer but at the same time must not cause undue manufacturing difficulties.

In addition to the above requirements, the error in any temperature interval must not exceed 5 percent of the nominal value of the interval. The intent of this requirement is to eliminate thermometers having large corrections of alternating signs, which would lead to uncertainties in the interpolation of scale corrections between calibration points.

Tables 4 and 5 also give suitable values for the subdivisions and the accuracy which may be expected. The word "*accuracy*" used in these tables refers to the best values attainable in the use of the thermometer when all corrections are applied. The final columns state the decimal figures to which the corrections are given for thermometers calibrated by the Bureau. They are stated to somewhat higher precision than can be attained with certainty in calibrating the thermometers. They are so-stated to avoid the possibility of an additional uncertainty due to rounding off.

6.2. Partial-Immersion Thermometers

In many instances it is required to measure temperatures under conditions where it is inconvenient or impossible to use a liquid-in-glass thermometer at total immersion. For such uses partial-immersion thermometers are designed with scales graduated to indicate true temperatures when the thermometers are immersed to specified depths. No stem temperature correction is necessary, therefore, when these thermometers are used with the same depth of immersion and emergent-stem temperature for which they are calibrated. Unless otherwise stated, each Report of Calibration issued by the Bureau gives corrections that apply for the temperatures prevailing above the comparison baths. When such a thermometer is to be used with a different stem temperature, the necessary emergent stem correction must be calculated as shown in section 5.4.c.

The accuracy attained with this type of thermometer will usually be significantly less than that possible with total-immersion thermometers. This is particularly the case when partial-immersion thermometers are used with stem temperatures greatly different than the temperature being measured. An unsteady or irreproducible environment surrounding the emergent stem, together with the inherent difficulty of estimating or measuring the emergent-stem temperature with sufficient accuracy, can contribute markedly to the uncertainty of a given thermometer indication. For this reason tables 6 and 7 show that accuracies expected of partial-immersion thermometers are not so high as those for total-immersion thermometers nor are the calibration corrections stated so precisely.

6.3. Low-Temperature Thermometers

The lowest temperature to which a mercury-filled thermometer can be used is limited by the freezing point of mercury at −38.9 °C (−38.0 °F). This limit may be extended to considerably lower temperatures by alloying thallium with the mercury. The eutectic alloy of 8.5 percent of thallium by weight has a freezing point of −59 °C (−74 °F) and is used successfully in thermometers for temperatures down to about −56 °C (−69 °F). The freezing temperature of the alloy is critically affected in the neighborhood of the eutectic by the amount of thallium present. Small differences in composition, resulting in either too much or too little thallium, have the effect of markedly raising the freezing point of the alloy. It is therefore difficult to achieve the lowest freezing temperature in practice. In addition, some thermometers with this filling have been found to behave erratically in the range of about two degrees above the freezing point. Consequently, thermometers of this type should not be used below −56 °C.

TABLE 6.—*Tolerances for Celsius partial-immersion mercury thermometers*

Temperature range in degrees	Graduation interval in degrees [a]	Tolerance in degrees	Accuracy [b] in degrees	Corrections stated to
Thermometers not graduated above 150 °C				
0 up to 100	1.0 or 0.5	1.0	0.1 to 0.3	0.1
0 up to 150	1.0 or 0.5	1.0	0.1 to 0.5	0.1
Thermometers not graduated above 300 °C				
0 up to 100	1.0	1.0	0.1 to 0.3	0.1
Above 100 up to 300	1.0	1.5	.5 to 1.0	.2
Thermometers graduated above 300 °C				
0 up to 300	2.0 or 1.0	2.5	0.5 to 1.0	0.5
Above 300 up to 500	2.0 or 1.0	5.0	1.0 to 2.0	.5

TABLE 7.—*Tolerances for Fahrenheit partial-immersion mercury thermometers*

Temperature range in degrees	Graduation interval in degrees [a]	Tolerance in degrees	Accuracy [b] in degrees	Corrections stated to
Thermometers not graduated above 300 °F				
32 up to 212	2.0 or 1.0	2.0	0.2 to 0.5	0.2
32 up to 300	2.0 or 1.0	2.0	0.2 to 1.0	0.2
Thermometers not graduated above 600 °F				
32 up to 212	2.0 or 1.0	2.0	0.2 to 0.5	0.2
Above 212 up to 600	2.0 or 1.0	3.0	1.0 to 2.0	.5
Thermometers graduated above 600 °F				
32 up to 600	5.0 or 2.0	5.0	1.0 to 2.0	1.0
Above 600 up to 950	5.0 or 2.0	10.0	2.0 to 3.0	1.0

[a] Partial-immersion thermometers are sometimes graduated in smaller intervals than shown in these tables, but this in no way improves the performance of the thermometers, and the listed tolerances and accuracies still apply.

[b] The accuracies shown are attainable only if emergent stem temperatures are closely known and accounted for.

Other low-temperature thermometers are commonly filled with organic liquids. While not considered to be as reliable as mercury-thallium-filled thermometers, they serve to extend the range below −56 °C. Some of these liquids are used as low as −200 °C (−328 °F).

Alcohol, toluene, and pentane have all been used as fluids for low-temperature thermometers. All of these fluids, however, have limitations of one kind or another. Other organic liquids, alone or in mixtures, have been found by some manufacturers to show better characteristics for particular applications.

All of these organic liquids have the disadvantage of wetting the bore of the thermometer tubing which may lead to significant error in the indications of such thermometers if sufficient precautions are not taken. Any liquid that wets the tube will leave a film on the wall as the meniscus falls, the thickness of the film being dependent among other things on the viscosity of the liquid, the interfacial action between the liquid and glass, and the rate at which the thermometer is cooled. Where possible the rate of cooling should be slow with the bulb cooled first. In this way the viscosity of the filling fluid in the thermometer bore is kept as low as possible until the final temperature is reached, thus minimizing the amount of liquid left behind on the wall. Even so, sufficient time should be allowed for drainage from the wall to be essentially completed. Under adverse conditions it may take an hour or more before the effect of drainage ends.

In addition to good drainage characteristics, a satisfactory low-temperature fluid should be free of water, dirt, or other foreign material which will separate out at temperatures for which the thermometer is graduated. Furthermore, low-temperature thermometers are frequently designed for use up to room temperature or above. In these cases the vapor pressure of the filling liquid becomes important. A low vapor pressure is necessary to prevent distillation of the liquid at the higher temperatures. Any dye added to improve the visibility of the thermometer liquid should be chosen for good color fastness with respect to light exposure or chemical action with the thermometer liquid.

Tolerances applicable to low-temperature thermometers are given in tables 8 and 9.

6.4. Beckmann Thermometers

A metastatic, or Beckmann thermometer is usually of the enclosed-scale type, so constructed that portions of the mercury may be removed from, or added to, the bulb permitting the same thermometer to be used for differential measurements in various temperature ranges. The scales are kept short, usually to 5 or 6 deg C, although some micro types have a scale of only 3 deg C. The "setting" of such a thermometer refers to the temperature of the bulb when the reading is 0° on the scale. When the setting is changed to allow for use at a higher or lower temperature, the quantity of mercury affected by a temperature change is different. It follows that two equal changes in temperature at different settings cause different indications on the scale. Therefore a "setting factor" must always be used to convert reading differences into true temperature differences whenever the thermometer is used at any setting different from the one at which its scale was calibrated. These setting factors combine corrections for the different changes in volume of different quantities of mercury during equal temperature changes, and the difference between the mercury-in-glass scale and the International Practical Temperature Scale.

Table 10 lists setting factors calculated for thermometers of Jena 16^{III} glass, or its American equivalent, Corning normal. The scale calibrations for Beckmann thermometers as reported by the Bureau are applicable to a setting of 20 °C, and the factor is consequently 1.0000 at this temperature. For a setting of any other temperature the observed temperature difference must be multi-

TABLE 8.—*Tolerances for low-temperature total-immersion thermometers*

Temperature range in degrees	Type of thermometer	Graduation interval in degrees	Tolerance in degrees	Accuracy in degrees	Corrections stated to
Celsius thermometers					
−35 to 0	Mercury	1 or 0.5	0.5	0.1 to 0.2	0.1
−35 to 0	do	.2	.4	.02 to .05	.02
−56 to 0	Mercury-thallium.	.5	.5	.1 to .2	.1
−56 to 0	do	.2	.4	.02 to .05	.02
−200 to 0	Organic liquid.	1.0	2.0	.2 to .5	.1
Fahrenheit thermometers					
−35 to 32	Mercury	1 or 0.5	1.0	0.1 to 0.2	0.1
−35 to 32	do	.2	0.5	.05	.02
−69 to 32	Mercury-thallium.	1 or .5	1.0	.1 to .2	.1
−69 to 32	do	.2	0.5	.05	.02
−328 to 32	Organic liquid.	2 or 1.0	3.0	.3 to .5	.2

TABLE 9.—*Tolerances for low-temperature partial-immersion thermometers*

Temperature range in degrees	Type of thermometer	Graduation interval in degrees	Tolerance in degrees	Accuracy in degrees	Corrections stated to
Celsius thermometers					
−35 to 0	Mercury	1.0 or 0.5	0.5	0.2 to 0.3	0.1
−56 to 0	Mercury-thallium.	1.0 or .5	.5	.2 to .3	.1
−90 to 0	Organic liquid.	1.0	3.0	.4 to 1.0	.2
Fahrenheit thermometers					
−35 to 32	Mercury	1.0 or 0.5	1	0.3 to 0.5	0.1
−69 to 32	Mercury-thallium.	1.0 or .5	1	.3 to .5	.1
−130 to 32	Organic liquid.	2 or 1	5	.8 to 2.0	.5

plied by the appropriate factor from the table. An example is given below the table.

In a common design of the Beckmann thermometer the large bulb is joined to the fine capillary, backed by the milk-glass scale, by a capillary of much larger diameter. When such an instrument is used at partial immersion this large capillary is a source of some uncertainty, since the temperature of this relatively large quantity of mercury, enclosed in the glass case, cannot be actually measured. When an estimate can be made of the temperature of the emergent stem, however, a correction may be calculated as described in section 5.4.e.

Tolerance requirements for Beckmann thermometers are given in table 11.

Under the heading "Accuracy of interval in degrees" is given the estimated accuracy attainable in the measurement of any interval within the limits of the scale.

No tolerances for scale error are given although it is desirable that the scale error be no greater than 0.02 °C over a 1.0 °C interval.

TABLE 10.—*Setting factors for Beckmann thermometers*

Setting	Factor	Setting	Factor
°C		°C	
0	0.9934	55	1.0096
5	.9952	60	1.0107
10	.9969	65	1.0118
15	.9985	70	1.0129
20	1.0000	75	1.0139
25	1.0015	80	1.0148
30	1.0030	85	1.0157
35	1.0044	90	1.0165
40	1.0058	95	1.0172
45	1.0071	100	1.0179
50	1.0084		

As an illustration, suppose the following observations were made:

Setting=25°C. Lower reading=2.058°
Stem temperature=24° Upper reading=5.127°

	Lower	*Upper*
Observed reading	=2.058	5.127
Correction from certificate	=+0.005	−0.008
Corrected upper reading		5.119
Corrected lower reading		2.063
Difference		= 3.056
Difference multiplied by setting factor (1.0015)		= 3.061
Emergent stem correction (see accompanying-stem correction sheet)		=+.004
Corrected difference		= 3.065

TABLE 11.—*Tolerances for Beckmann and calorimeter thermometers*

Type of thermometer	Graduation interval in degrees	Allowable change in correction in degrees	Accuracy of interval in degrees	Corrections stated to
Beckmann	0.01 °C	0.01 over 0.5° interval for setting of 20 °C	0.002 to 0.005	0.001
Bomb calorimeter	.01 °C	0.02 over 1.5° interval	.005 to .01	.002
Do	.02 °C	0.02 over 1.5° interval	.005 to .01	.002
Do	.05 °F	0.04 over 2.5° interval	.01 to .02	.005
Gas calorimeter	.1 °F	0.15 over a 5° interval	.02 to .05	.02

6.5. Calorimeter Thermometers

Calorimeter thermometers include a specialized group of etched-stem mercury-in-glass thermometers which are used for accurate differential measurements. Since the accuracy of these thermometers at any one temperature is of less importance than the accuracy of the temperature intervals, no reference point is required.

Table 11 gives the scale tolerances required of some typical calorimeter thermometers. No tolerances for scale error are given although it is desirable that the scale corrections be no larger than about five graduation intervals.

7. Thermometer Design

To be eligible for calibration the thermometer shall be of good design, material, and workmanship and shall be permanently marked with a serial number which will uniquely identify the thermometer with its Report of Calibration. No attempt is made to list specifically all possible

defects of design and workmanship, since some latitude for judgment must be reserved for individual cases as they arise. Certain important requirements of general applicability can be singled out, however, and these are described below.

7.1. Materials of Construction

While the cleanliness of the thermometer bulb, bore, and liquid filling have a pronounced effect upon the performance of a finished thermometer, of equal importance is the proper choice of the glass from which the thermometer is manufactured. Particularly, the thermometer bulb must be made of glass suitable for use in the temperature range for which the thermometer is graduated. In addition, the thermometer must be adequately annealed so that continued use will not greatly change its indications. This is especially important for a thermometer graduated above 300 °C or 600 °F. The quality of the thermometer glass and the adequacy of the annealing process may be judged in part by the stability of reference-point readings (such as ice points).

A method of test for bulb stability is described in The American Society for Testing and Materials' Method E77.

Table 12 lists some types of glasses commonly used in the manufacture of thermometer bulbs with reasonable upper temperature limits of their use. These estimates by Thompson [8] are based upon the work of Liberatore and Whitcomb [9], whose results show that significant changes in bulb volume may occur if the bulb is heated for long periods of time at a temperature higher than 130 °C (234 °F) below the strain point of the glass. Thermometers may be used intermittently, however, up to within 70 °C (126 °F) of the strain point of the bulb glass. The strain point of a glass is defined as that temperature at which the glass has a viscosity of $10^{14.5}$ poises [10].

It should be noted that the use of glass with a high strain point, such as that of borosilicate glass or higher, result in better thermometer performance and stability even in thermometers used at temperatures much lower than the exposure limits given in table 12.

TABLE 12.—*Temperature exposure limits for various thermometer glasses*[a]

	Strain point	Exposure limits			
		Continuous		Intermittent	
	°C	°C	°F	°C	°F
Corning normal 7560	500	370	700	[b]430*	[b]805*
Kimble R 6	490	360	680	420	790
Jena 16 III	495	365	690	425	795
Corning borosilicate 8800	529	400	750	460	860
Jena borosilicate 2954	548	420	790	480	900
Corning 1720	668	540	1005	600	1110
Jena Supremax 2955	665	535	995	595	1100

[a] From reference [8].
[b] *405 °C or 760 °F if Corning Standard Thermometer 0041 glass is used for the stem.

All high-temperature thermometers should be filled with a dry inert gas under sufficient pressure to prevent separation of the mercury at any temperature for which the scale is graduated. Total-immersion thermometers graduated above 150 °C or 300 °F must be gas filled to minimize the distillation of mercury from the top of the column. Gas filling for lower temperatures is optional, but is strongly recommended.

7.2. Scale Design and Workmanship

Thermometers of the solid-stem type shall have the graduation marks etched directly on the stem and so located as to be opposite the enamel back. In thermometers of the enclosed-scale type, the graduated scale must be securely fastened to prevent relative displacement between scale and and capillary (for example, by fusing the scale to the enclosing tube) or, if this is not done, a mark should be placed on the outer tube to locate the scale and indicate at any time whether the scale is in its original position. The graduation marks shall be clear cut, straight, of uniform width, and in a plane perpendicular to the axis of the thermometer.

The scale shall be graduated either in 1.0-, 0.5-, 0.2-, or 0.1-deg intervals, or in decimal multiples of such intervals. The divisions shall be numbered in such a way that the identification of any graduation is not unnecessarily difficult. Thermometers with scales graduated in 0.25-deg intervals, or in 0.25-deg intervals further subdivided, are sometimes difficult to read and their elimination is desirable. Thermometers graduated in 0.1- or 0.2-deg intervals, or decimal multiples of these, should have every fifth mark longer than the intermediate ones and should be numbered at every tenth mark. Thermometers graduated in 0.5-deg intervals, or in decimal multiples of 0.5 deg, require three lengths of graduation marks consisting of alternating short and intermediate marks, with every tenth mark distinctly longer the others, and numbering at every 10th or 20th mark.

The scale must not be extended to temperatures for which the particular thermometer glass is unsuited. For example, a thermometer of borosilicate glass graduated to 500 °C (932 °F) would be ruined in a short time if used at that temperature.

7.3. Scale Dimensions

Coarse graduation marks do not represent good design. Optimum line width, however, depends in some measure upon the use for which a particular thermometer is intended. If the thermometer indications are to be observed precisely, for example to 0.1 division, the width of the graduation marks in the extreme case should not be more than 0.2 of the interval between center lines of the graduations. In cases where the thermometer

must be read quickly or in poor light, and less precision is expected, somewhat wider lines may be acceptable.

In addition, the graduation marks must not be too closely spaced. The closest permissible spacing depends upon the fineness and clearness of the marks. In no case should the distance between center lines of adjacent graduation marks on an etched-stem thermometer be less than 0.4 mm. The minimum permissible interval between graduation marks for an enclosed-scale thermometer is 0.3 mm if the lines are ruled on a milk-glass scale; for other scales the minimum is 0.4 mm. The minimum in no case represents good design, and well-designed thermometers will have graduation intervals considerably larger than the specified minimum.

In order that a thermometer scale be usable over its entire range, graduation marks must not be placed too close to any enlargement in the capillary. Insufficient immersion of the mercury in the main bulb or a capillary enlargement, graduation marks placed over parts of the capillary that have been changed by manufacturing operations, or graduations so close to the top of the thermometer that excessive gas pressure results when the mercury is raised to this level, may lead to appreciable errors. The following distances between graduations and the bulb and between graduations and enlargements in the bore are considered as minimum limits commensurate with good thermometer design:

(a) A 13-mm length of unchanged capillary between the bulb and the lowest graduation, if the graduation is not above 100 °C (212 °F); a 30-mm length if the graduation is above 100 °C (212 °F).

(b) A 5-mm length of unchanged capillary between an enlargement and the graduation next below, except at the top of the thermometer.

(c) A 10-mm length of unchanged capillary between an enlargement, other than the bulb, and the graduation next above, if the graduation is not above 100 °C (212 °F); a 30-mm length if the graduation is above 100 °C (212 °F).

(d) A 10-mm length of unchanged capillary above the highest graduation, if there is an expansion chamber at the top of the thermometer; a 30-mm length if there is no expansion chamber. For the purposes of this requirement, "an expansion chamber" is interpreted as an enlargement at the top end of the capillary bore which shall have a capacity equivalent to not less than 20 mm of unchanged capillary.

7.4. Reference Point on Scale

Thermometers graduated above 150 °C or 300 °F, or precision thermometers expected to be used with an accuracy better than 0.1 °C or 0.2 °F, when calibrated for the measurement of actual temperatures rather than temperature differences, must have a reference point at which the thermometer can be conveniently retested from time to time. From these reference-point tests, the effects of changes in bulb volume on the thermometer indications may be followed throughout the life of the thermometer and the proper corrections applied at any time. If no suitable reference point such as the ice or steam point is included in the range of the main scale, a short auxiliary scale including a fixed point shall be provided. To avoid making the thermometer unduly long, a contraction chamber may be introduced between the auxiliary scale and the main scale. The graduations on an auxiliary scale must extend for a short interval both above and below the reference point. Similarly, when the main scale ends near a temperature to be used as a reference point, the graduations must be continued for a short interval above or below the reference point as the case may be.

Any auxiliary scale must have graduations identical to those of the main scale, both dimensionally and in terms of temperature.

Reference points are not needed on thermometers intended for differential measurements (such as calorimeter thermometers) nor on thermometers not graduated above 150 °C or 300 °F if these are not to be calibrated to an accuracy better than 0.1 °C or 0.2 °F.

7.5. Marking of Partial-Immersion Thermometers

Partial-immersion thermometers will not be calibrated unless plainly marked "partial immersion", or its equivalent (for example, "76-mm immersion"), and unless a conspicuous line is engraved on the stem to indicate the depth to which the thermometer is to be immersed. This mark must not be less than 13 mm above the top of the bulb. Special partial-immersion thermometers adapted to instruments which fix definitely the manner for use (for example, viscometers and flash-point testers in which the thermometer is held in a ferrule or other mounting fitting the instrument) need not be marked, although it is always desirable that the thermometers be marked "partial-immersion".

8. Special Notes

The following brief notes on the characteristic behavior of mercury-in-glass thermometers are added to aid the user in understanding the behavior of such thermometers and in a better utilization of the information contained in the Reports of Calibration.

8.1. Glass Changes

The changes which occur in thermometer bulb glass on heating to a temperature, high but still within its intended range of use, and subsequent cooling to ambient are an involved function of

time and temperature and will depend upon the thermal history of the glass, both during manufacture and previous use, the time of exposure to the high temperature, and the rate of cooling. Evidence from many investigations [9, 11, 12] seems to show that when a glass is held indefinitely at some fixed temperature, density (and volume) changes proceed more or less slowly toward a preferred density corresponding to a quasi equilibrium condition characteristic of the particular kind of glass and the temperature. Since these changes involve molecular rearrangements, they proceed more rapidly at high temperatures where the viscosity of the glass is lower and the molecular mobility consequently higher. Thus a close approach to quasi equilibrium may be reached in the order of hours at annealing temperatures, while infinite time may be required at much lower temperatures. As a consequence, when a glass is cooled in the order of minutes from some high temperature, equilibrium is not reached at lower temperatures on the way down, and an equilibrium density more nearly corresponding to the high temperature is "frozen" into the glass. This characteristic behavior of glass has a lasting effect on the performance of liquid-in-glass thermometers. For its entire lifetime, a thermometer may retain a "memory" of its thermal history at the higher temperatures experienced during manufacture. The techniques of good manufacture, therefore, are designed to produce in the thermometer glass a state which will result in maximum stability at the temperature of use. The achievement of perfect stability for all conditions of use, however, is not possible in thermometer manufacture so that changes in ice point readings with time and use are observed. The changes observed in scale readings at the ice point reflect changes of the same magnitude and sign at all points on the scale since they are the result of changes in bulb volume; changes in the stem have very little effect.

The changes in bulb volume are of two kinds resulting naturally from the behavior of glass as discussed above.

a. Temporary Changes

Upon heating to high temperature the bulb expands from its initial state and, after a short period of time, appears to reach an equilibrium condition corresponding to that particular high temperature If the thermometer is then cooled sufficiently slowly through critical temperature regions, the glass will return to close to its initial state, and the ice point reading will show no change on this account. If, on the other hand, the thermometer is cooled rapidly as, for example, cooling naturally in still air, the bulb will retain a portion of its expanded condition, and the ice point reading will be *lower* than its reading before the heating. This phenomenon is known as "zero, or ice-point depression". Thermometers which have been heated to high temperatures recover from this ice-point depression in an unpredictable way, and frequently there will be no significant recovery after a year's time at room temperature. The ice-point depression has a reproducible value, however, for a thermometer cooled in still air, so that the ice point, taken from time-to-time immediately (within about 1 hour) following cooling in this manner, may be used reliably to show changes in thermometer bulb volume with time and use.

On the other hand, thermometers used only up to about 100 °C will usually exhibit a relatively rapid recovery from the ice-point depression, and the original bulb volume will be recovered within the equivalent of 0.01 or 0.02 deg C in about 3 days. This phenomenon has an important bearing on the precision attainable with mercury thermometers and most be taken into consideration in precision thermometry, especially in the interval 0 to 100 deg C. Thus, if a thermometer is used to measure a given temperature, it will read lower than it otherwise would if it has a short time previously been exposed to a higher temperature. With the better grades of thermometric glasses the error resulting from this hysteresis will not exceed (in the interval 0 to 100 deg) 0.01 of a degree for each 10-deg difference between the temperature being measured and the higher temperature to which the thermometer has recently been exposed and with the best glasses only a few thousandths of a degree for each 10-deg difference. The errors due to this hysteresis become somewhat erratic at temperatures much above 100 °C. For the reasons briefly set forth above it is customary, in precision thermometry, to apply a scale correction based upon an ice point reading taken immediately after the temperature measurement.

b. Permanent Changes

A second type of change in thermometer glasses, known as the "secular change," results in a non-recoverable decrease in bulb volume which may progress with time even at room temperature, but which is markedly accelerated at high temperatures. This type of change is evidenced by an *increase* in the ice point reading. At low to moderate temperatures there may be a gradual change which will continue for years. With better grades of thermometer glasses the change will not exceed 0.1 °C in many years, provided the thermometer has not been heated to temperatures above about 150 °C. In addition, permanent changes in bulb volumes have sometimes been observed with thermometers which have been repeatedly cycled at low temperatures, for example between −30 and +25 °C [13]. At high temperatures the secular change usually progresses more rapidly at first, but, with continued heating, tends toward lower rate of change with time. The rate of secular change will be dependent upon the kind of glass used in the thermometer bulb and the particular heat treatment given the thermometer in manufacture. Thermometers manu-

factured according to good practices will evidence only small secular changes, but thermometers made of glass unsuitable for the use temperature, or improperly annealed, may show changes as large as 20 °C (36 °F) after continued heating at high temperature [14].

In the use of high-temperature thermometers care must be taken to avoid overheating. In only a few minutes of heating at a temperature higher than the intended range of the thermometer, the built up gas pressure above the liquid column may cause a permanent distortion of the bulb resulting in lower thermometer indications.

8.2. Pressure Effects

Since glass exhibits elastic properties, the volume of a thermometer bulb will change with change of pressure, either internal or external. Therefore, at the same temperature, the reading of a thermometer in a horizontal position will be different than its reading in a vertical position. Thermometer readings will change also with altitude or when the external pressure is changed in some other way. Changes of about 0.1 °C (0.2 °F) per atmosphere have been found for many thermometers with bulb diameters between 5 and 7 mm. This value can be used with some confidence for estimating the probable effect of an external pressure change. The effect of change of internal pressure is about 10 percent greater. Formulas for both external and internal pressure coefficients have been derived by Guillaume [15].

If the external pressure coefficient β is defined as the change in scale reading in degrees resulting from a change of 1 mm Hg in external pressure, Guillaume found the relation,

$$\beta_e = k \frac{R_e^2}{R_e^2 - R_i^2},$$

where R_e and R_i are external and internal radii of the bulb, and k is a constant containing elastic properties of the glass and a conversion factor for expressing the volume change in terms of change of thermometer reading in degrees. For Celsius thermometers, Guillaume found a value of 5.2×10^{-5} degrees C/mm Hg for k, but Hall and Lever [7], by experiment, found a value about 25 percent lower for their thermometers.

In cases where an accurate correction is necessary, β_e should be determined experimentally. A simple apparatus for the determination is shown in figure 9.

The internal pressure coefficient β_i is more difficult to determine accurately but may be calculated from β_e by means of the relation,

$$\beta_i = \beta_e + 1.5 \times 10^{-5},$$

for thermometers in Celsius degrees, or

$$\beta_i = \beta_e + 2.7 \times 10^{-5}$$

for Fahrenheit thermometers.

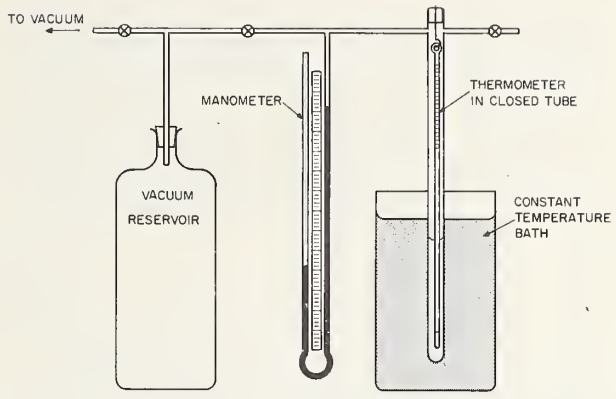

FIGURE 9.—*Apparatus for measurement of the external pressure coefficient.*

8.3. Lag

Practically all theoretical treatments of the question of thermometer lag are based on the assumption that Newton's law of cooling (i.e., that the rate of change in the reading of the thermometer is proportional to the difference between thermometer temperature and bath temperature) holds for the thermometer. It is an immediate consequence of this law that when a thermometer is immersed in any medium it does not take up the temperature immediately, but approaches it asymptotically. A certain time must elapse before the thermometer reading agrees with the temperature of the medium to 0.1 deg, still longer to 0.01 deg, the temperature remaining constant. If the temperature is varying, the thermometer always indicates, not the true temperature, but what the temperature of the medium was at some previous time. The thermometer readings are thus said to "lag" behind the temperature by an amount which may or may not be negligible, depending upon the rapidity of temperature variation and the physical characteristics of the thermometer. A more complete treatment of this subject has been given by Harper [16].

For a thermometer immersed in a bath, the temperature of which is changing uniformly, the lag may be defined as the interval in seconds between the time when the bath reaches a given temperature and the time when the thermometer indicates that temperature. This lag λ is dependent upon the dimensions and material of the thermometer bulb, the medium in which it is immersed, and the rate at which this medium is stirred. For instance, the lag when in the still air of a room would be perhaps 50 times that of the same thermometer when immersed in a well-stirred water bath.

Since the value of λ for mercurial thermometers is not large, being from 2 to 10 sec on a well-stirred water bath, it is not generally necessary to correct for it. For example, if two thermometers, one having a lag of 3 and another of 8 sec, are read simultaneously in a bath whose temperature is rising at the rate of 0.001 degree in 5 sec, the

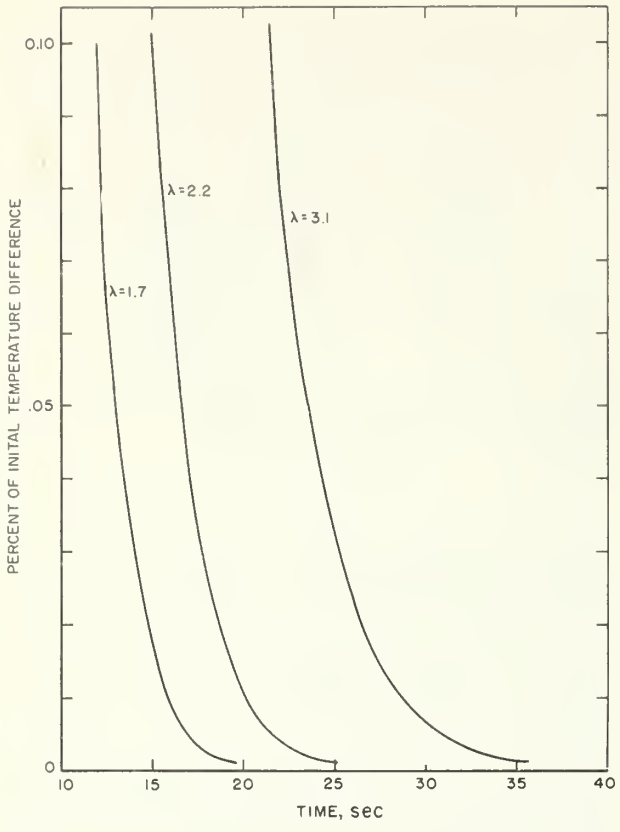

FIGURE 10.—*The approach to temperature in a stirred water bath for three thermometers with typical lag constants.*

former will read 0.001 degree higher than the latter, due to the lag. In the intercomparison of thermometers the rate of temperature rise may nearly always be kept so small that this lag correction is negligible.

If a thermometer at a given initial temperature is plunged into a bath at a different temperature, the lag, λ, is the time required for the original difference in temperature between thermometer and bath to be reduced to $1/e$ (that is 1/2.7) of itself. In a length of time 4 λ the difference will have become about 1.5 percent and in a length of time 7 λ about 0.1 percent of the original difference. Determinations of λ for solid stem laboratory thermometers representative of American manufacture have yielded values of about 2 to 3 seconds in a well-stirred water bath. Figure 10 shows the approach of thermometer readings to the water bath temperature for 3 selected thermometers having different values of λ. For example, if the thermometer for which λ=2.2 sec is initially at 25 °C and then is immersed in a bath at 75 °C, the thermometer reading will be within 0.05 °C (0.1 percent of 50 °C) of the bath temperature in 15 sec and within 0.01 °C in 19 sec. The curve for λ=3.1 was obtained for an American Society for Testing and Materials (ASTM) specification 56C calorimeter thermometer with a bulb diameter (outside) of 7.9 mm and bulb length of 44 mm. The value of λ=2.2 was found for an ASTM 7C thermometer having bulb dimensions of 5.4 by 12 mm. The third curve, for λ=1.7, was obtained for a bulb with dimensions of 5.4 by 34 mm. It is probable that most solid stem thermometers of American manufacture will have values of λ lying within the range covered by the 3 curves shown.

According to Harper [16] the value of λ for a given thermometer in a well stirred oil bath will be about twice its value for a water bath.

When a thermometer is used to measure changes of temperature, as in calorimetry, it has been shown by White [17] that the lag enters into the observations in such a way as to be eliminated from the results in applying the usual radiation corrections. Therefore the lag need not be considered, provided only that the initial and final readings are made when the temperature is varying uniformly. This is not strictly true, however, in the case of some Beckmann thermometers that have no true value of λ, as has been explained in the paper referred to above.

8.4. Separated Columns

Many inquiries are received concerning separated mercury columns, particularly after shipment. Since no means of avoiding such occurrences has yet been found, some directions for joining the mercury may be helpful. The mercury may separate somewhat more readily in thermometers which are not pressure-filled, but it can be more easily joined since there is little gas to separate the liquid. The process of joining broken columns consists of one or a series of manipulations which may be effective, and these are briefly described here.

(a) The bulb of the thermometer may be cooled in a solution of common salt, ice, and water (or other cooling agent) to bring the mercury down into the bulb. Moderate tapping of the bulb on a paper pad or equally firm object or the application of centrifugal force usually serves to unite the mercury in the bulb. If the salt solution does not provide sufficient cooling, carbon dioxide snow (dry ice) may be used. Since the temperature of dry ice is about −78 °C (−108 °F) and mercury freezes at about −40 °C (−40 °F) it will cause the mercury to solidify. Care must be taken to warm the top of the bulb first so that pressures in the bulb due to the expanding mercury may be relieved.

(b) If there is a contraction chamber above the bulb or an expansion chamber at the top of the thermometer the mercury can sometines be united by warming the bulb until the column reaches the separated portions in either enlargement. Great care is necessary to avoid filling the expansion chamber completely with mercury, which might produce pressures large enough to burst the bulb. Joining the mercury is more readily accomplished if the quantity in either cavity has first been shattered into droplets by tapping the thermometer laterally against the hand.

(c) As a last resort, especially for thermometers having no expansion chambers, small separated portions of the column can sometimes be dispersed by warming into droplets tiny enough to leave space for the gas to by-pass, and then droplets can then be collected by a rising mercury column.

The procedure for thermometers in which organic liquids are used is similar. Liquids in the stem can more readily be vaporized and may then be drained down the bore. The latter process is aided by cooling the bulb. All of these manipulations require patience, and experience is helpful, but they will yield results if care is used. A convenient method of ascertaining that all the liquid has been joined is a check of the ice point, or some other point on the scale.

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